Vibrational Spectroscopy of Size-Selected Sodium-Doped Water Clusters[†]

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The vibrational OH stretch spectra have been measured for $Na(H_2O)_n$ clusters in the size range from $n = 8$ to 60. The complete size selection is achieved by coupling the UV radiation of a dye laser below the ionization threshold with the tunable IR radiation of an optical parametric oscillator. The spectra are dominated by intensity peaks around 3400 cm^{-1} which we attribute to an increased transition dipole moment of delocalized electrons in this type of doped cluster. Aside from the positions of free (3715 cm^{-1}) and double donor (3560 cm^{-1}) bonds which are known from pure water clusters, specific transitions are observed at 3640 cm^{-1} and in the range of the single donor bonds between 3000 and 3200 cm^{-1}.

I. Introduction

Experiments with neutral clusters of atoms or molecules are difficult to conduct with completely size-selected clusters. There are two reasons for this behavior. On one hand, the most commonly used cluster sources, the supersonic, adiabatic expansion, and the gas aggregation in cold gas flows, generate usually a distribution of sizes.[1] On the other hand, the size-selective detection process by ionization and subsequent selection in a mass spectrometer is hampered by severe fragmentation processes.[2] This is especially valid for van der Waals, hydrogen, and ionic bound systems in which the neutral and ionized interaction potentials are shifted appreciably against each other and eventually highly excited vibrational states are reached in the ionization processes which lead to the mentioned evaporation.[3] Therefore, special experimental methods are needed to label the neutral cluster sizes in an unambiguous way. One possibility is the momentum transfer in a single collision experiment with atoms.[4,5] This method is, however, restricted to small sizes of about $n = 13$ because of resolution problems.[6] Another possibility is to attach an aromatic chromophore molecule to the cluster and to ionize it by a two color resonant two photon process which is, by choosing the right wavelength, nearly fragmentation free.[7−11] This method requires special electronic transitions and is also limited to about the same sizes. In addition, it contains the aromatic molecule as a perturber. A new type of labeling was recently introduced by the soft argon-mediated electron attachment to vibrationally excited neutral water clusters.[12]

In the present contribution, we will introduce a new method which will allow us to measure IR spectra for completely size-selected molecular clusters without any restriction in the size domain. The applied method is as follows: In the course of our work for measuring unambiguously size distributions of weakly bound clusters, we found that a convenient way to solve this problem is to dope the clusters with one Na atom and to ionize the complete system by a single photon.[13,14] Working closely above the threshold, a nearly fragmentation free detection is achieved, since for metals the neutral and ionic potential curves are quite similar and are usually not shifted against each other. The method was applied to ammonia and water clusters[13] and the rare gas clusters argon, krypton, and xenon[14] as well. Because of the low ionization energy of sodium, which is even lower in combination with water and ammonia, the atoms or molecules in the cluster with their much higher ionization potentials are not affected. This scheme is now used for complete size selection as is shown in Figure 1. The photon energy is lowered slightly below the threshold. Then together with the IR photons the energetic constraint for ionization is again fulfilled and the ion can be detected in a mass spectrometer as an enhancement of the signal when the IR laser is turned on. The procedure works provided that sufficient coupling occurs between the vibrational and the electronic motion of the ionization. This is an interesting aspect in itself. The scheme is completely size selective and covers, in principle, the whole range from very small to more than thousands of molecules, whatever can be generated in the source. We have applied the method first to $Na(H_2O)_n$ clusters. Similar ideas have been used in the vibrational spectroscopy of single aromatic molecules. In one case, the ionizing transitions are accomplished by coupling the IR laser radiation with a two photon laser transition.[15,16] In the other example, the IR radiation of a free electron laser and a single UV photon are applied.[17] The authors claim that the necessary coupling between the vibration and ionization is caused by an enhanced ionization probability in vibrational excited states or simply by intramolecular vibrational energy redistribution and addition of energies, respectively. A further experiment is reported on the spectroscopy of a Rydberg series of Ar atoms where the synchrotron radiation is coupled with IR photons for the ionization.[18]

II. Experimental Section

The experiments were carried out in a molecular beam machine which has been described in detail elsewhere.[14] Therefore, we will present here only a short account of the main parts with emphasis on those that have been changed. The machine consists of a source chamber, a buffer chamber, and a detector unit. In a first step, the water clusters are produced by expanding water vapor of 0.53 bar seeded in helium at 4 bar through a nozzle of conical shape with a diameter of 63 μm, an opening angle of 41°, and a length of 2 mm. These clusters are doped by a single sodium atom by passing the beam through a

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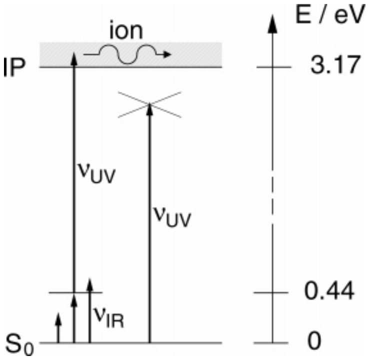

Figure 1. Schematic diagram of the excitation mechanism.

pick-up cell which is placed in the buffer chamber and kept at a pressure of 0.023 mbar. The clusters are detected by a reflectron time-of-flight mass spectrometer. The ionization is carried out by the photons of a dye laser pumped by an excimer laser with a pulse width of 28 ns. Under optimal conditions, a mass resolution of $m/\Delta m = 1600$ was obtained at $m = 200$ u, based on a drift length of 1820 mm. The ions are extracted in the direction of the beam and detected on a microsphere plate. The mass spectra are sampled using a digital storage oscilloscope in special particle counting mode. The spectra are corrected for the size dependence of the detection probability and the ionization cross section, the transformation from time to mass coordinates, and double ionization processes. The average size of the $Na(H_2O)_n$ clusters was measured to be $\langle n \rangle = 30$ under the above-mentioned source conditions. The pick-up method leads temporarily to a heating of the cluster by collisions with the dopant. But simulations of this process for rare gases at temperatures of 300 K show that the cluster rearranges to a large extent to the original structure at a temperature of 32 K.[19] In the present experiment, the temperature of the Na vapor is 490 K but the binding energies are more than a factor of 10 larger than those for the rare gases so that we would expect no change of the cluster temperature in the range of 60 K.[20] The isomers, however, which are formed by the interaction with the Na atom preferably at the surface of the cluster, are not necessarily the energetically lowest ones.

The IR radiation used to excite the clusters is obtained from a Nd:YAG laser pumped optical parametric oscillator (OPO) in the spectral range from 2900 to 3800 cm^{-1}.[21,22] It consists of a master oscillator containing a $LiNbO_3$ crystal, which is pumped by the fundamental of a Nd:YAG laser. The master oscillator is seeded by the narrow-bandwidth IR radiation obtained by difference frequency mixing the output of a pulsed dye laser and the 532 nm radiation of the same Nd:YAG laser in a $LiIO_3$ crystal. The typical output energy for the low-frequency component (idler) is ≥ 4 mJ per pulse in the entire spectral range covered in this study. The pulse width is 10 ns. The bandwidth of the IR radiation, which is determined by the bandwidth of the dye laser, is chosen to be 0.5 cm^{-1}. We note that the wavenumber region between 3480 and 3510 cm^{-1} cannot be reached in the experiment caused by water impurities in the crystal. The time synchronization of the two laser beams is achieved by triggering the IR laser by a pulse delay generator. The UV pulse of the ionization laser is time delayed by about 80 ns with respect to the IR laser. This value is adjusted by optimizing the enhancement signal.

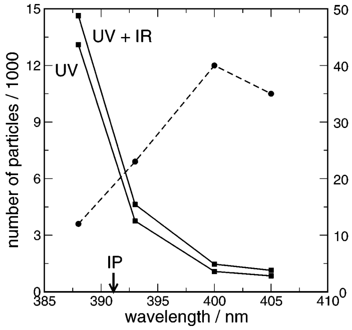

Figure 2. Signal with and without IR radiation. Scale on the left side: number of ionized particles without and with IR radiation. Scale on the right side (dashed line): the difference signal as enhancement in percent.

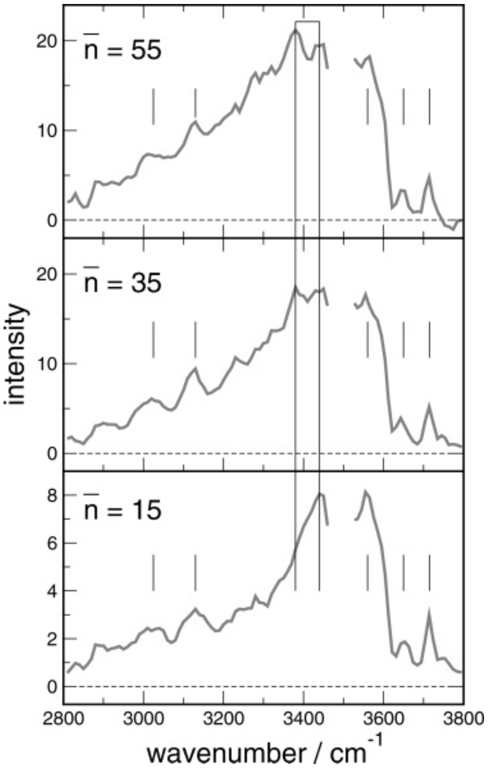

Figure 3. Measured OH stretch spectrum of $Na(H_2O)_n$ clusters. The spectra are summed over $n \pm 5$ sizes of the ones indicated by $\bar{n}$. The long lines indicate the transition caused by the delocalized electrons, for the origin of the short lines see text.

III. Results and Discussion

In a first series of experiments, we have tried to find the optimal conditions for running this double resonance experiment. The ionization potential for $Na(H_2O)_n$ clusters for $n \geq 4$ is 3.17 eV (391 nm).[23] We have measured the signal with the IR radiation off and on as function of the dye laser wavelength. The percentage enhancement signal is obtained by dividing the difference signal $N - N_0$ by N_0. The results for the fixed IR wavenumber of 3550 cm^{-1} are displayed in Figure 2. As expected, the signal increases close to the threshold. The signal enhancement which is the difference between these two signals increases slightly and reaches a maximum at 400 nm. With increasing intensity in the threshold region, it drops to small values. Thus, we will run further experiments at 400 nm of the dye laser and scan the frequency of the IR laser. The results for selected cluster sizes are presented in Figure 3. To obtain an overview of the general trends, we have averaged the spectra of 10 single sizes with equal weights. Therefore, the mean sizes $\bar{n} = 15 \pm 5$, $\bar{n} = 35 \pm 5$, and $\bar{n} = 55 \pm 5$ should not be mixed up with the average sizes of the log-normal distributions presented in experiments without size selection which usually

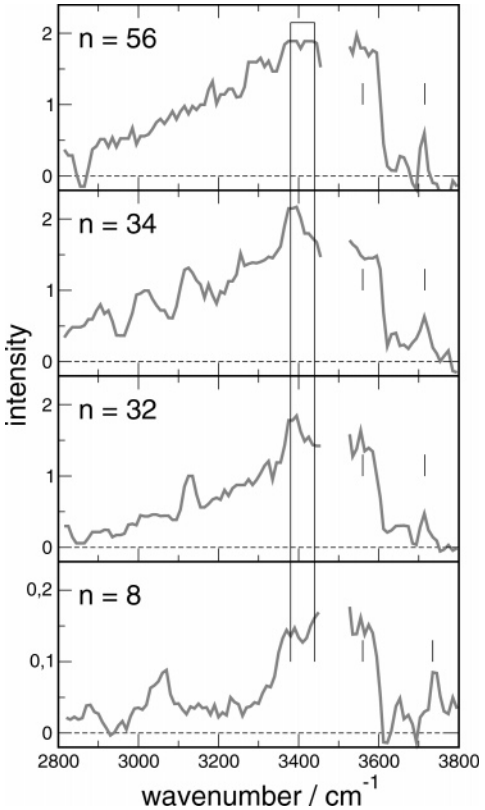

Figure 4. Measured OH stretch spectrum of selected $Na(H_2O)_n$ clusters for the sizes indicated. The long lines indicate the transition caused by the delocalized electrons; the short lines mark the transitions based on the free and the DDA bonds which are already known from the pure water clusters.

extend to much larger sizes with a half width which corresponds to the average value. All spectra are dominated by the peak around 3400 cm^{-1} which is marked by the double line. At higher wavenumbers there are peaks at 3550, 3640, and 3715 cm^{-1} which are more or less the same for the selected sizes. At the low energy range, we observe mainly peaks at 3120 and 3020 cm^{-1}. They are most pronounced in the spectrum for $\bar{n} = 35$ and nearly disappear for $\bar{n} = 55$. Also, the main peak slightly shifts from above 3400 cm^{-1} for $\bar{n} = 15$ to below 3400 cm^{-1} for $\bar{n} = 55$. The latter spectrum is also much broader and shows less structures than the other two. Figure 4 exhibits the results for single size-selected clusters for $n = 8$, 32, 34, and 56. While all four spectra roughly agree in the peaks from 3400 cm^{-1} onward, differences mainly show up below 3200 cm^{-1}, exhibiting one peak, two peaks, or no peaks.

From what is known from the analysis of pure, large water clusters[24] and model calculations[25] in this size range as well as from calculations of small water clusters[26] and the similar system $Na^+(H_2O)_n$ up to $n = 20$,[27,28] we can attribute the bands at 3715 and 3560 cm^{-1} to the free OH and the three-coordinated double donor, single acceptor (DDA) OH bond, respectively. They are marked by short lines in Figure 4. The band at about 3640 cm^{-1} is new and has never been observed in pure water clusters. It is attributed to a terminal water molecule with a double acceptor AA or a single acceptor A with a further bond to the Na atom. These arrangements have been observed in the calculations of small $Na(H_2O)_n$ clusters[29−31] and their ionic variants.[28] The bands in the region below 3200 cm^{-1} are certainly caused by single donor DAA or DA bonds which are known to undergo the largest red shifts. The individual positions depend sensitively on the exact environment, and their complete explanation has to wait until calculations for this very system are available. There remains the interpretation of the peak with the largest intensity around 3400 cm^{-1} marked by the drawn-through lines. This is definitely the region of four-coordinated molecules which becomes more and more important with increasing cluster size. The amazing point, however, is that this peak is also present in very small systems where the number of DDAA molecules is zero or quite small. A possible explanation has been given by Mundy et al.[29] in the interpretation of the reaction of sodium with water clusters. In the course of this work, they calculated the electronic structure of $Na(H_2O)_6$ using Car−Parrinello molecular dynamics at 100 K. The 3s electrons were spread over a large area of nearly 3 Å and were thus distributed over several of the solvating water molecules. These authors remark in a side note that this extended dynamic state gives rise to a very active IR mode. We think that we observe exactly this mode in our experiments. In fact, the preliminary calculation of the spectrum for $Na(H_2O)_4$ using the autocorrelation function of the dipole moment gives a large peak at 3370 cm^{-1}.[32] The presence of these delocalized electrons also explains the coupling of the vibrational motion to the ionization process which manifests itself in the presence of the peak around 3400 cm^{-1} in all our spectra.

This interpretation is supported by recent experiments of the vibrational spectroscopy of water anions $(H_2O)_n^-$ carried out by the group of Johnson[33] in continuation of previous work on these systems.[34] They observed in their argon-mediated predissociation and photodetachment data the binding motif of a single water molecule through a double H-bond to the electron cloud which leads to a pronounced double peak at 3400 and 3260 cm^{-1} in the OH stretch spectra of the smaller clusters. This pattern moves gradually to smaller wavenumbers with increasing cluster size.[35] In the sodium-doped water clusters, we mainly observe only one peak at 3400 cm^{-1}. This can be explained by the higher possibility to form only one H-bond to the electron cloud in a cluster environment in which also the counterion Na^+ is present. Indeed, an inspection of some calculated structures[29,31] reveals the presence of these single bonds. Whether the increase of the intensity around 3300 cm^{-1} with increasing cluster size is due to DDAA molecules or the shift observed in the negatively charged water clusters cannot be decided without calculations. We close with the statement that the intensity at 3400 cm^{-1} which is also present at small cluster sizes is caused by the delocalized electrons.

IV. Conclusions

In conclusion, we have presented an experimental method which allows us to take the vibrational spectra of a completely size-selected neutral cluster in a range between $n = 8$ to 60 that was previously not accessible. This was achieved by coupling the UV photons of a dye laser at 400 nm, below the threshold for ionization with the IR radiation of a tunable OPO. In this manner, the $Na(H_2O)_n$ clusters were ionized and an enhancement of the ion signal was observed. The spectra, taken in the OH stretch region, exhibit a series of characteristic features which indicate the coordination of the molecule and which are partly known from the analysis of pure water clusters. In addition, further characteristic features appeared in the spectra which are attributed to the perturbation of the Na atom and manifest themselves in different coordinations (3640 cm^{-1}) or delocalized electrons (3400 cm^{-1}). The latter result is confirmed by recent experiments with negatively charged water clusters.[33]

The method is quite general provided that a reasonable coupling occurs between the vibrational and electronic motion.

It is not restricted in size and can be extended to any size which can be generated in the source and detected in the mass spectrometer. It requires a tunable light source close to the ionization threshold. In the present case we have, for convenience, chosen a system with a quite low ionization potential of 3.17 eV. With the availability of new XUV and synchrotron sources, the method can be extended to a large amount of other systems. It thus opens up new possibilities for systematic investigations in any size range. It should be especially suited for systems in which charge separation occurs, since such a process will foster the coupling of the vibrational and the electronic motion.

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